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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002951005 for a patent by CURTIN UNIVERSITY OF TECHNOLOGY and SHELL GLOBAL SOLUTIONS INTERNATIONAL B.V. as filed on 27 August 2002.

I further certify that the above application is now proceeding in the name of SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. pursuant to the provisions of Section 113 of the Patents Act 1990.



WITNESS my hand this
Twentieth day of October 2003

J. Billingsley

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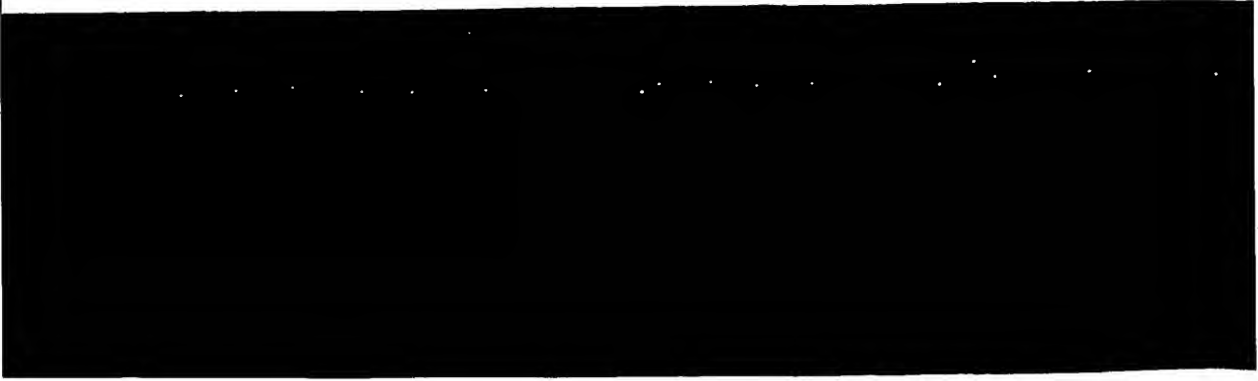
PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

**"METHOD OF REMOVING SOLID CARBON DIOXIDE FROM
CRYOGENIC EQUIPMENT"**

The invention is described in the following statement:-



METHOD OF REMOVING SOLID CARBON DIOXIDE FROM
CRYOGENIC EQUIPMENT

Field of the Invention

- 5 The present invention relates to a method of removing solid CO₂ from cryogenic equipment and more particularly relates to cryogenic equipment used in the production of Liquefied Natural Gas (LNG).

Background to the Invention

- 10 Natural gas contains a wide range of species which are capable of forming solids during the cryogenic process of producing Liquid Natural Gas (LNG) known as liquefaction. One of the species that causes considerable problems to LNG producers is carbon dioxide (CO₂). In a conventional LNG facility, pre-treatment of the natural gas is conducted to decrease the CO₂ content to between 50 and 125 ppm prior to the natural gas entering the
15 liquefaction process.

- On average, CO₂ compositions in a natural gas feed stream can range between 0.5% and 30% and can be as high as 70% in commercially viable reservoirs like Natuna. CO₂ is typically removed using chemical reactions such as reversible absorption processes with
20 amine solvents. This is an expensive and complex process and commonly encounters operational problems such as foaming, corrosion, blocked filters, amine degradation, and losses of amine, water and hydrocarbons are commonly encountered. The process also consumes energy to regenerate and pump the solvent.

- 25 In conventional LNG plants, the natural gas is typically cooled in one or more heat exchangers. If insufficient CO₂ is removed prior to the natural gas entering the heat exchangers, CO₂ precipitates as a solid and accumulates on the cold surfaces of the heat exchangers and other plant equipment eventually rendering these items inoperable. When fouling has reached a sufficient level, the vessel must be taken off-line for the CO₂
30 solids to be removed. In the process of defouling equipment, the vessel, baffles and/or pipework may be damaged, which only encourages further fouling in the next production cycle. Moreover, solids condensing on metal surfaces form an insulating film reducing the thermal efficiency of the heat exchanger.

There is a need for a simpler, more economical process for the removal of solid CO₂ which has fouled plant equipment under cryogenic conditions.

- 5 Throughout this specification the term "comprising" is used inclusively, in the sense that there may be other features and/or steps included in the invention not expressly defined or comprehended in the features or steps subsequently defined or described. What such other features and/or steps may include will be apparent from the specification read as a whole.

10

Summary of the Invention

According to one aspect of the present invention, there is provided a method of removing solid CO₂ from cryogenic equipment, the method comprising the steps of:

- 15 (a) introducing a stream including ethane to said cryogenic equipment to convert solid CO₂ to liquid form whereby a mixture of liquid ethane and liquid CO₂ is formed; and
- (b) removing the mixture of liquid ethane and CO₂ from the cryogenic equipment.

- 20 According to another aspect of the present invention, there is provided a method of removing CO₂ fouling of cryogenic equipment containing LNG, the method comprising the steps of:

- (a') removing the LNG from the said cryogenic equipment;
- (a) introducing a stream including ethane to convert solid CO₂ to liquid form
- 25 whereby a mixture of liquid ethane and liquid CO₂ is formed; and
- (b) removing the azeotropic mixture of liquid ethane and liquid CO₂ from the cryogenic equipment whereby the cryogenic equipment is defouled of solid CO₂ and available for the reintroduction of the LNG stream.

- 30 Preferably, the method comprises the step of adjusting the relative percentages of ethane and CO₂ for a given pressure and temperature such that the mixture of ethane and CO₂ is azeotropic. The fastest and most efficient dissolution of CO₂ solids occurs under these conditions.

Preferably the stream including ethane is a liquid.

5 Preferably, the method further comprises the step of separating the azeotropic mixture of liquid ethane and CO₂ to form a first product rich in ethane and a second product rich in CO₂. More preferably, the first product rich in ethane is available for recycling to step (a). More preferably, the second product rich in CO₂ is also recovered and recycled.

10 The method of separating the azeotropic mixture may include distillation or membrane-based separation techniques or a combination thereof.

The method may include the step of introducing one or more alkanes or their isotopes to the azeotropic mixture prior to the separation step. The addition of one or more alkanes or their isotopes has the effect of widening the two-phase liquid vapour equilibrium area
15 in the ethane-CO₂ system to allow easier separation of ethane and CO₂ from the azeotropic ethane-CO₂ liquid mixture.

Preferably, the cryogenic equipment is selected from the list including heat exchangers, pipes, storage vessels, sub-cooling vessels and/or separators.

20

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

25

Figure 1 is a vapour-liquid phase equilibrium diagram for a typical natural gas feed stream with the composition shown in Table 1.0.

Figure 2 is the vapour-liquid phase equilibrium diagram for the same natural gas feed stream to which additional CO₂ has been added to bring the total CO₂ to 25%.

30

Figure 3 is the vapour-liquid phase equilibrium diagram for the same natural gas feed stream composition for which the CO₂ content has been adjusted to 15%.

Description of the Preferred Embodiments

The present invention derives from observations made during a series of tests conducted using a cryogenic vessel known as the Sapphire Cell. The Sapphire Cell as the name suggests is constructed of pure single crystal sapphire and allows hitherto impossible
5 direct observation of the phenomena occurring during LNG liquefaction. Based on their observations of these phenomena, the applicant has realised that liquid ethane can be used to remove CO₂ fouling of cryogenic equipment.

10 It is known that ethane and CO₂ form an azeotrope. An azeotrope forms because of a particular molecular interaction between two or more components. When such components are mixed, the vapour and liquid compositions at equilibrium are equal within a given pressure and temperature range. The formation of an azeotrope is usually seen to introduce an obstacle for the separation of the two components within the liquid mixture and is thus something that is typically avoided in chemical processing plants.

15 During testing, the Sapphire Cell was used as a flash vessel in fluid communication with a cryogenic chamber. Natural gas was introduced to the Sapphire Cell and flashed down to 20 bar at -82°C whereby LNG was formed. Under the conditions at which liquefaction takes place, the CO₂ still present in the natural gas feed stream will
20 precipitate out in solid form within the flash vessel.

The LNG produced was stored in the cryogenic chamber and the system was cooled down to -80°C using a multi-component refrigerant system with liquid nitrogen down to -161°C. The cryogenic chamber was maintained at the same pressure as the flash vessel
25 until equilibrium conditions were attained so that the vapour-liquid equilibrium phase diagrams for a given range of compositions could be generated.

The liquid level within each of the flash vessel and cryogenic chamber was measured using simple volumetric calibration. The liquid level within the Sapphire Cell could also
30 be observed by the eye through the transparent walls of the Cell. The temperature of the system was monitored using temperature sensors inside each of the chambers with a third temperature sensor monitoring the air bath around the cryogenic chamber and flash vessel. Pressure sensors were located outside the air bath at the inlet and outlet of each of

the cryogenic chamber and the flash vessel. Multi-port sampling valves were provided for each of the cryogenic chamber and flash vessel to allow on-line gas chromatographic analysis of samples when desired.

- 5 The system was agitated using a vortex operated magnetically until solid separation of the CO₂ was observed. The vortex encouraged gravity separation of the more dense CO₂ solids to the bottom of the chamber. The effect of creating a vortex is to draw the solids formed within the vessel towards the wall of the vessel where they migrate down towards the bottom of the vessel. The vortex can be established by mechanical means using a
- 10 stirrer or by including a hydrocyclone at the base of the vessel.

In the first series of tests natural gas of known composition as outlined below in Table 1.0 was introduced through a control valve into the Sapphire Cell.

15

Table 1.0 GC Analysis of the Feed Gas*

	Component	Mole Fraction
1	N ₂	2.54
2	CO ₂	2.39
3	C ₁	84.16
4	C ₂	7.08
5	C ₃	3.05
6	IC ₄	0.31
7	NC ₄	0.38
8	IC ₅	0.05
9	NC ₅₊	0.04

*(Gas includes ppm's of Mercaptan)

In a second series of tests, additional CO₂ was added to the chamber to bring the CO₂ content up to 25% as outlined below in Table 2.0.

Table 2.0 GC Analysis of the Feed Gas with Addition of Extra CO₂*

	Component	Mole Fraction
1	N ₂	1.939
2	CO ₂	24.95
3	C ₁	64.64
4	C ₂	5.493
5	C ₃	2.385
6	IC ₄	0.239
7	NC ₄	0.292
8	IC ₅	0.038
9	NC ₅₊	0.023

*(Gas includes ppm's of Mercaptan)

- 5 LNG was transferred into the cryogenic storage vessel leaving behind a slush comprising a relatively small percentage of LNG plus solid CO₂ crystals in the flash vessel. The composition of the LNG produced during the liquefaction process is outlined below in Table 3.0. From this table it can be seen that the CO₂ composition has been reduced from 25% in Table 2.0 to just 0.29% due to the successful removal of CO₂ solids.

10

Table 3.0 GC Analysis of the Produced LNG After CO₂ Separation at 10 bar -140°C

	Component	Mole Fraction
1	N ₂	1.28
2	CO ₂	0.29
3	C ₁	94.65
4	C ₂	4.48
5	C ₃	2.02
6	IC ₄	0.21
7	NC ₄	0.27
8	IC ₅	0.04
9	NC ₅₊	0.03

CO₂ content was increased to 30% in the original gas composition shown in Table 1.0.

- 15 The flash vessel containing the slush was left for one hour to achieve equilibrium. Liquid ethane was introduced at the same conditions of -80°C and 26 bar. It was observed that the solid CO₂ within the slush started to dissolve immediately as liquid ethane was introduced.

In a third series of tests, an azeotrope of 15% CO₂ and 85% ethane was introduced into

Method of removing carbon dioxide from cryogenic equipment

the Sapphire Cell. The contents of the Sapphire Cell were agitated using the magnetically induced vortex. The transparent walls of the Sapphire Cell made it possible to observe the fine solid crystals of CO_2 forming and dissolving in rapid succession.

- 5 The present invention is directed towards using this observed phenomenon in a commercially useful way to remove CO_2 fouling from cryogenic plant equipment. As outlined above, the introduction of ethane traditionally would be avoided because of the known azeotrope that forms between ethane and CO_2 .
- 10 In the first preferred embodiment of the present invention, a heat exchanger or other cryogenic pipework fouled with CO_2 is taken off-line. Liquid ethane is then introduced into the heat exchanger or pipework. The CO_2 solids dissolve as they convert back to liquid form. The fastest rate of dissolution has been observed to occur when the ethane and CO_2 are present in sufficient relative amounts at a given pressure and temperature to
- 15 form an azeotropic mixture. Under azeotropic conditions, dissolution of the CO_2 solids is observed to happen at its greatest speed and with greatest efficiency.

Having introduced the ethane and converted the solid CO_2 to liquid form, it is preferable for the mixture of ethane and CO_2 to be separated to recover and recycle the ethane.

20

- The most common method of separating homogeneous liquid mixtures is the use of distillation, ie repeated vaporisation and condensation whereby the vapour phase gradually becomes enriched in the more volatile component. However, separation of a liquid mixture by distillation depends on the fact that even when a liquid is partially
- 25 vaporised, the vapour and liquid compositions differ. The vapour phase becomes progressively more enriched in the more volatile component and is depleted in the less volatile component. Repeated partial vaporisation is used to achieve the desired degree of separation. An azeotrope, however, cannot be separated using ordinary distillation since little enrichment of the vapour phase occurs with each partial vaporisation step.
- 30 Therefore in most cases, azeotropic liquid mixtures require special methods to facilitate separation of the component species.

Separation of the azeotropic mixture may be effected using techniques such as extraction, absorption, crystallisation, decanting, multi-stage extraction or other chemical treatments or any combination thereof. In order to use distillation in either a continuous or batch operation, it may be necessary to add an entrainer such as propane, butane or other
5 suitable alkane or a combination thereof, the choice being dependent on the particular phase behaviour of the system and available compounds. It is envisaged that the alkane or alkanes would be recovered and recycled to the system also.

Alternatively, membrane separation methods may be used prior to or independently of
10 distillation. Such methods include dialysis, reverse osmosis, ultra-filtration, electrodialysis, helium separation through glass, hydration separation through palladium and alloy membranes, immobilised solvents and/or liquid-surfactant membranes. The driving force for separation using membranes is either a pressure or concentration difference across the membrane. Membranes may be used to break azeotropic mixtures
15 prior to feeding the mixture to a subsequent continuous or batch distillation separation process.

To identify the most favourable distillation sequences, the vapour-liquid phase equilibrium diagrams were generated for a range of compositions of CO₂ and ethane.
20 Figure 1 shows the measured vapour-liquid phase equilibrium diagram for the natural gas feed stream with the composition shown in Table 1.0. Figure 2 is the vapour-liquid phase equilibrium diagram for the natural gas feed stream with the composition shown in Table 2.0, where the total percentage of CO₂ has been increased to 25%.

25 Figure 3 is the vapour-liquid phase equilibrium diagram for a mixture of 15% CO₂ and 85% ethane. It is readily apparent from Figures 3 when compared to Figures 1 and 2 that there is very little separation between the vapour phase boundary and the liquid phase boundary in Figure 3. This type of narrow two-phase envelope is typical of an azeotropic mixture.

30

The widest separation between the vapour phase boundary and the liquid phase boundary in Figure 3 is observed at 0°C and 30 bar. These would be the temperature and pressure conditions that would need to be applied using a separation means such as distillation. In

the case of Figure 2, there is a much wider range of temperature and pressure conditions available to achieve separation by distillation.

In the second preferred embodiment of the present invention, the method can be used for removing solid CO₂ from cryogenic equipment used in the production of LNG. The LNG would first be drained from the system before introducing liquid ethane in the manner outlined above.

A series of tests conducted using the Sapphire Cell have confirmed that the presence of methane in the natural gas feed stream has little or no effect on the formation of CO₂ solids during LNG liquefaction nor the subsequent dissolution of the CO₂ solids when the ethane is introduced.

It is proposed that this method of removing CO₂ contaminants could be used for pipelines for carrying LNG, heat exchangers, cryogenic cooling vessels, and any other plant equipment used under cryogenic conditions where CO₂ fouling occurs.

It will be readily apparent to a person skilled in the relevant art that the present invention has significant advantages over the prior art including, but not limited to, the following:

20

- (a) Existing LNG plants can be defouled without any requirement for modification of the plant equipment;
- (b) Recycling of the ethane will significantly contribute to reducing the cost of applying the method according to the present invention for the removal of the CO₂ solid contaminants;
- (c) The process is applicable to a wide variation of feed gas compositions; and
- (d) The CO₂ content of the natural gas can be adjusted in order to assist in the removal of the CO₂ solids by the ethane.

25

30 Now that the present invention has been described in detail, it will be apparent to those skilled in the relevant arts that numerous modifications and variations may be made without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of

which is to be determined from the foregoing description.

DATED this 27th day of August 2002

5 CURTIN UNIVERSITY OF TECHNOLOGY AND SHELL GLOBAL SOLUTIONS
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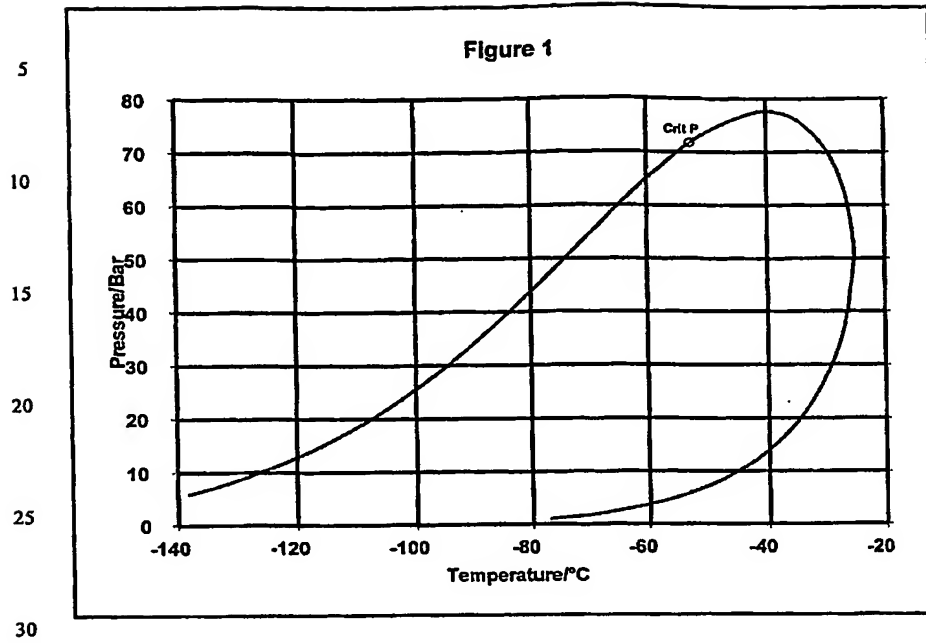
By their Patent Attorneys

GRIFFITH HACK

Fellows Institute of Patent and Trade Mark

10 Attorneys of Australia

Method of removing carbon dioxide from cryogenic equipment



Method of removing carbon dioxide from cryogenic equipment

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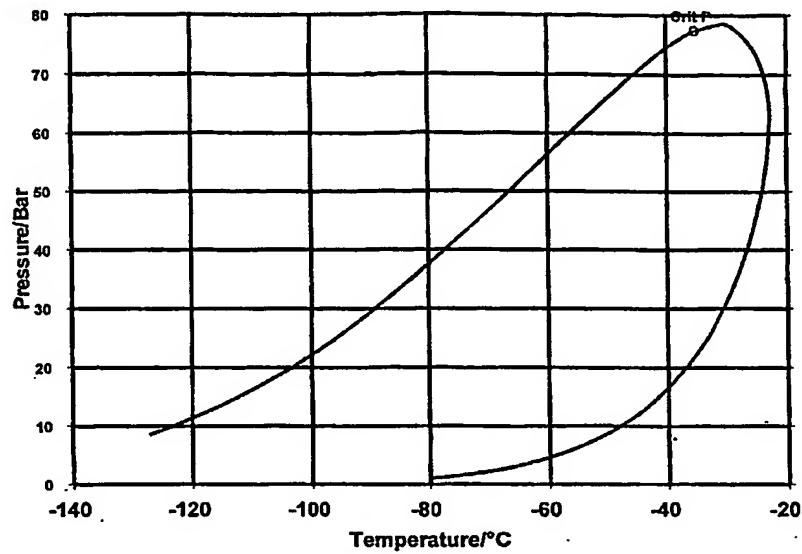
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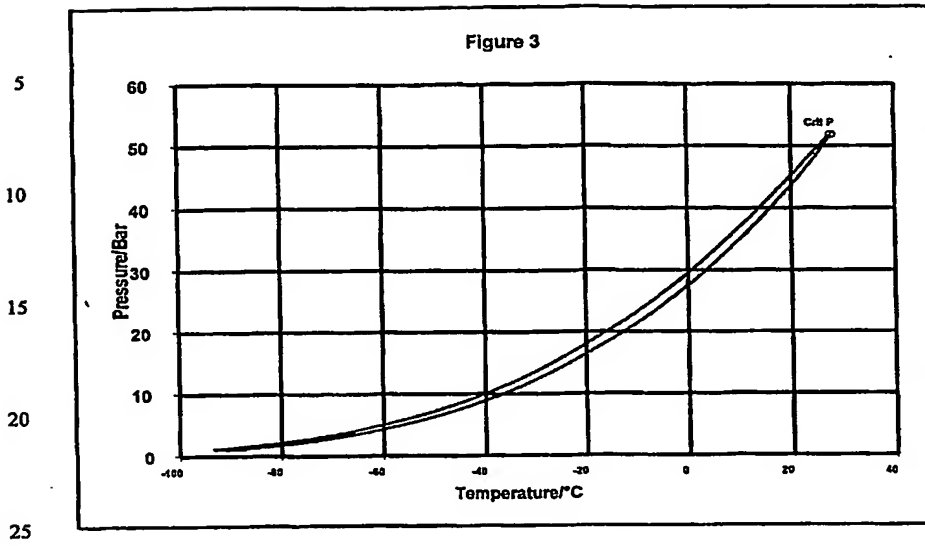
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Figure 2



Method of removing carbon dioxide from cryogenic equipment



Method of removing carbon dioxide from cryogenic equipment

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